



## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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<b>(21) International Application Number:</b> PCT/SB94/00018 <b>(22) International Filing Date:</b> 6 October 1994 (06.10.94) <b>(30) Priority Data:</b> P-9300529 7 October 1993 (07.10.93) SI <b>(71) Applicant (for all designated States except US):</b> KRKA, TOVARNA ZDRAVIL, P.O. [SI/SI]; Cesta Herojev 45, 68000 Novo Mesto (SI). <b>(72) Inventors; and</b> <b>(75) Inventors/Applicants (for US only):</b> KORNHAUSER, Aleksandra [SI/SI]; Skapinova 19, 61000 Ljubljana (SI). KRUMPAK, Aleksandra [SI/SI]; Stritarjeva 7, 63250 Rogaska Slatina (SI). ŠKERLAJ, Vojko [SI/SI]; Hubadova 12, 61000 Ljubljana (SI). POKORNY, Miroslav [SI/SI]; Cankarjeva 11, 68000 Novo Mesto (SI). <b>(74) Agent:</b> PATENINA PISARNA, .D.O.O.; Čopova 14, 61000 Ljubljana (SI).		<b>(81) Designated States:</b> AU, BG, BR, BY, CA, CN, CZ, HU, JP, KR, NO, NZ, PL, RO, RU, SK, UA, US, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), ARIPO patent (KE, MW, SD, SZ).  <b>Published</b> <i>With international search report.</i>
<b>(54) Title:</b> PESTICIDE COMPOSITION AND USE THEREOF		
<b>(57) Abstract</b>  A non-toxic biodegradable pesticide composition comprising as an active substance a modified starch having the reduction number between 2 and 10, preferably between 4 and 7, which is the product of an acid/thermic hydrolysis of natural starches, especially potato starch, with interruption of the hydrolysis by rapid cooling; a surfactant for regulating adhesion and a preservative is disclosed.		

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## **Pesticide Composition and Use Thereof**

### ***Technical Field***

The present invention belongs to the field of plant protection and relates to a non-toxic biodegradable pesticide composition using specially prepared polysaccharides of homoglycane or heteroglycane type, especially modified starch polymers and/or derivatives thereof, which composition exhibits an insecticide, acaricide and fungicide action.

### ***Prior Art and Technical Problem***

In the protection of plants against pests several groups of insecticides, acaricides and fungicides are used. Chemical insecticides, acaricides and fungicides are the most well-known and widely used. They are advantageous due to a rapid and effective action. The long-term use thereof, however, is restricted due to the following negative effects:

- the phenomenon of the resistance of pests to chemical agents for plant protection and, consequently, the use of higher and higher concentrations of the available agents and a constant need for novel kinds of pesticides;
- killing of useful predatory insects resulting in an additional destroying of ecological balance;
- a long waiting time (a long period between the application of a pesticide and the permitted use of an agricultural product), which especially inhibits the production and eating of vegetables;
- a high acute and chronic toxicity representing a risk for users of protective agents and for consumers of agricultural products;
- environmental pollution, especially of water and soil.

Due to the above reasons a definite trend towards limiting the use of chemical pesticides is noticeable. It is to be expected that in the future chemical pesticides will be used only in very restricted concentrations and in specific cases. Chemical agents

having a physical action are also used, which agents, however, are potentially phytotoxic and represent substances harmful to the environment.

#### *Technical Solution*

It has been found in our investigations that polysaccharides, especially modified starch polymers and/or derivatives thereof, when prepared in a special way exhibit a special stickiness in aqueous solutions, which gave rise to the idea of using solutions thereof for controlling insects, mites and fungi. Experiments showed that such agents have a pesticide action, however, the action thereof is especially physical (mechanical), i.e. after application by spraying, a sticky film is formed on the surface of pests, which makes vital functions such as movement, breathing and propagation impossible. Pesticides so prepared are biologically degradable derivatives of natural compounds. Pests do not develop a resistance thereto, they are not generally phytotoxic and are quite non-toxic for humans and animals as a rule, which makes possible the use thereof in water reserve areas and in closed spaces (such as e.g. in greenhouses and for house plants) and there is no need for waiting time.

Thus the first object of the present invention is a non-toxic biodegradable pesticide composition comprising

- as an active substance a modified starch having the reduction number between 2 and 10, preferably between 4 and 7, which is the product of an acid/thermic hydrolysis of natural starches, especially potato starch, under interrupting the hydrolysis by rapid cooling;
- a surfactant for regulating adhesion and
- a preservative.

Modified starches used as active substances in pesticide compositions according to the invention are water soluble substances as a rule.

Modified starches having a lower reduction number are used in the preparation of foodstuffs, e.g. of custard additives. For these products the value of reduction number is not critical.

Acid/thermic hydrolysis is a standard technological process. It is carried out with an inorganic acid at a temperature between 150 and 200 °C and is interrupted as soon as the desired reduction number is achieved.

The addition of a preservative and a surfactant is useful for improving the properties of basic pesticide formulations.

Suitable preservatives are copper salts, especially copper sulfate, and standard organic preservatives such as sodium benzoate. The concentration of preservatives especially depends upon the kind thereof and upon the end use of a pesticide.

The purpose of adding a surfactant is especially the regulation of adhesion of sprayed drops onto biochemically different parts of pests and onto the cuticle of plants. Among the surfactants, alkyl aryl polyglycol ether derivatives are especially suitable. The concentration also depends upon the kind thereof and upon the end use of a pesticide.

The pesticide formulation for further use may be in the form of a dry substance or in the form of a real or of a colloidal (especially aqueous) solution. The stability of such a solution prepared according to the invention was tested and the results showed that after more than one year of storage at room temperature in closed plastic barrels no delamination and no settling down occurred.

The preferable pesticide formulation for the end use is a real or colloidal aqueous solution, preferably a 2 to 30% solution, especially a 6 to 20% solution. The main application route of the pesticide is spraying.

Such pesticide formulations are viscous and at spraying form fine droplets, which form a film on the surface of insects, which at drying makes the vital processes and activities of pests impossible.

Insects so treated have their wings, antennae and legs stuck together, their movement and breathing are rendered impossible. After drying the film of modified starch polymers and/or derivatives thereof becomes brittle and peels off the cuticle of plants together with dead insects and/or mites. The peeling of dried spray is faster at the technique of watering from the upper side.

The plant sprayed with the pesticide according to the present invention is not inhibited in its growth and development and in some cases the pesticide application also had a positive effect on the plant development. Such a phenomenon was observed in vine plants in littoral climate where the grape crop had a higher acid content and thus a higher quality. A possible cause for that phenomenon was a lower absorption of light due to the pesticide film, which resulted in a changed ratio between sugars and acids in the crop.

Pesticide formulations prepared according to the invention may also be used in the combination (a mixture or a solution) with small quantities (e.g. up to 0.5% with regard to the amount of the end form of the formulation to be applied) of standard (e.g. chemical) pesticides. In this application frequently a definite synergistic action of both agents occurs, whereby the biodegradable pesticide according to the invention still maintains its characteristic physical pesticide action. At a substantially reduced concentration of the chemical agent, the effect of controlling pests is greater under an additional prolonged action to pests. Advantages of such applications are a smaller consumption of toxic pesticides per hectare and their less frequent application under simultaneous higher efficacy of plant protection.

The activity of the novel biodegradable non-toxic pesticide having an insecticide, acaricide and fungicide effect and its activity in combination with standard (e.g. chemical) pesticides was demonstrated in fruit trees, vine, vegetables and ornamental plants against different kinds of pests e.g.:

- mites (e.g. *Tetranychus urticae*, *Panonychus ulmi*, *Calepitrimerus vitis*, *Tarsonemus palidus*),
- different kinds of plant lice (*Aphis* sp.),
- *Trialeurodes vaporariorum*,
- *Pseudococcus* sp.,
- *Coccus hesperidum*, *Quadraspidiotus perniciosus*,
- *Cydia pommonella*,
- *Lobesia botrana*, *Eupoecillia ambiguella*,
- *Botrytis cinerea*,
- *Plasmopara viticora*,
- *Uncinula necator*.

Another object of the present invention is thus the use of a pesticide composition according to the invention as a physico-mechanical pesticide having an insecticide, acaricide and fungicide action for controlling different kinds of plant pests.

A still further object of the present invention is a pesticide composition comprising a basic pesticide composition as defined above in the combination with chemical insecticides, acaricides and fungicides, which composition provides for a synergistic and prolonged action.

With the compositions according to the invention we succeeded in that any manipulation therewith was totally harmless to health while simultaneously excellent pesticide actions were achieved.

The invention is illustrated by the following Examples.

#### *Example 1*

##### **Preparation of a stable pesticide formulation**

The pesticide formulation according to the invention was prepared by blending the following ingredients in a stainless steel kettle at a temperature of about 35 °C:

	(%)
a pesticide according to the invention	30
as defined in the description	
SANDOVIT (Chromos, Zagreb) -	
surfactant	1
copper sulfate - preservative	0.005
water	to 100

#### *Example 2*

##### **Preparation of a stable pesticide formulation**

The procedure was the same as in Example 1 with the exception that 500 ppm of sodium benzoate were used as the preservative instead of copper sulfate.

*Example 3***Preparation of a stable pesticide formulation**

The procedure was the same as in Example 1 with the exception that RADOVIT (1%) (Radonja, Sisak, Croatia) was used as the surfactant instead of SANDOVIT.

*Example 4***Preparation of a stable pesticide formulation**

The procedure was the same as in Example 2 with the exception that RADOVIT (1%) (Radonja, Sisak, Croatia) was used as the surfactant instead of SANDOVIT.

*Example 5***Application against fruit mite (*Panonychus ulmi*)**

10% and 20% aqueous pesticide solutions prepared from the pesticide formulation according to Example 1 were applied to adult plants of gladiolus (*Gladiolus sp.*) and *Datura sp.* infested with fruit mite (*Panonychus ulmi*).

Both plants were grown in the greenhouse of the Agricultural Institute of Slovenia. Gladioli were grown in beds and *Datura sp.* as pot plants.

The efficiency of the application (calculation of efficiency) was measured according to Abbot's method. The testing showed a very high efficiency of application, i.e. a strong acaricide action of the pesticide. Table 1 shows the efficiency of the pesticide application on the fruit mite.

TABLE 1

agent	effect of pesticide on the fruit mite	
	gladiolus	<i>Datura</i>
20% pesticide	100.0%	100.0%
10% pesticide	100.0%	96.8%



*Example 6***Application against *Calepitrimerus vitis***

A 20% aqueous pesticide solution prepared from the pesticide formulation according to Example 1, was applied to adult plants of vine (*Vitis vinifera*) of the sort "Laški Rizling" infested with *Calepitrimerus vitis*.

Vine was grown in a commercial vineyard.

The efficiency of the application of the pesticide was established by a comparison between the length of internodes of test plants to which pesticide was applied, and control plants. The measurement was carried out at four different times.

The testing showed a great difference between the length of internodes of test plants and control plants, i.e. a very high efficiency of the application and a very strong acaricide action of the pesticide.

Table 2 shows the efficiency of the pesticide application on *Calepitrimerus vitis*.

TABLE 2

plant - vine	length of internodes (cm)				
	I	II	III	IV	average
20% pesticide applied	3.97	4.17	3.85	3.15	3.79
control	2.66	2.67	2.23	2.00	2.39

*Example 7***Application against plant lice (*Aphis sp.*) without chemical pesticides and in combination therewith**

There were used pesticide formulations as employed in Example 5, a 0.05% solution of the commercial chemical pesticide Actellic-50 (active substance pirimiphos-methyl, CA 29232-93-7) as well as a combination of a 10% pesticide solution according to the invention with the addition of 0.05% (with regard to the total amount of the test solution) of Actellic-50. The formulations were tested in greenhouses on adult plants of carnation (*Dianthus sp.*) and *Calceolaria rugosa* infested with plant lice (*Aphis sp.*).

The efficiency of the pesticide application was calculated according to Henderson-Tilton's formula.

The plants were infested with non-winged forms of plant lice. The pesticide showed a very good insecticide action. In previous testings still greater activity against winged forms had been observed. In the combination with Actellic-50 a definite synergistic action of both agents occurred.

Table 3 shows the efficiency of pesticide application to plant lice (non-winged forms).

**TABLE 3****Pesticide action on plant lice**

agent	carnation	Calceolaria
20% pesticide	54.9%	52.3%
10% pesticide	61.8%	45.1%
10% pesticide + 0.05% of Actellic-50	93.7%	52.5%
0.05% Actellic-50	82.6%	26.8%

*Example 8***Application against *Quadraspidiotus perniciosus* without chemical pesticides and in combination therewith**

There were used a 10% aqueous pesticide solution prepared from the pesticide formulation according to Example 1, a 0.3% solution of the commercial chemical pesticide Mitac-20 (active substance amitraz, CA 33089-61-1), a combination of a 10% solution of the pesticide according to the invention to which 0.3% of Mitac-20 was added, a 0.3% solution of the commercial chemical pesticide Basudin (active substance diazinon, CA 10311-84-9) as well as a 1.25% solution of the commercial chemical pesticide Ogriol. The formulations were tested on adult plants of apple tree (*Malus domestica*) of the sort "Jonathan", age 25 years, infested with *Quadraspidiotus perniciosus*.

The apple trees were grown in a test orchard of the Agricultural Institute of Slovenia.

The efficiency of the application (calculation of pesticide efficiency) was measured according to Abbot's method.

The testing showed an efficiency of the pesticide application (insecticide action) in comparison with commercial pesticides.

Table 4 shows the efficiency of the pesticide application to *Quadraspidiotus perniciosus*.

**TABLE 4**

agent	pesticide action on <i>Quadraspidiotus perniciosus</i> (%)
10% pesticide	54.9
10% pesticide + 0.3% of Mitac-20	56.7
0.3% Mitac-20	52.2
0.3% Basudin	69.5
1.25% Ogriol	50.5

*Example 9***Application against *Pseudococcus* sp.**

The pesticide formulation disclosed in Example 5 was applied to the adult plants of rubber plant (*Ficus benjamina*) infested with *Pseudococcus* sp.

The rubber plants were grown in a greenhouse.

The efficiency of the pesticide application was measured according to Henderson-Tilton's formula.

The testing showed a high efficiency of the pesticide application (insecticide action).

Table 5 shows the efficiency of the pesticide application to *Pseudococcus* sp..

TABLE 5

agent	pesticide action on <i>Pseudococcus</i> sp. (%)
20% pesticide	77.5
10% pesticide	67.5

*Example 10***Application against *Cydia pommonella* without chemical pesticides and in combination therewith**

There were used a 10% aqueous pesticide solution prepared from the pesticide formulation according to Example 1, a 0.3% solution of the commercial chemical pesticide Mitac-20 (active substance amitraz, CA 33089-61-1) as well as a combination of a 10% solution of the pesticide according to the invention to which 0.3% of Mitac-20 were added. The formulations were tested on adult plants of apple tree (*Malus domestica*) of the sort "Jonathan", age 25 years, infested with *Cydia pommonella*.

The apple trees were grown in a test orchard of the Agricultural Institute of Slovenia.

The efficiency of the application (calculation of efficiency) was measured according to Abbot's method.

The testing showed an efficiency of the pesticide application (insecticide action) in comparison with commercial pesticides.

Table 6 shows the efficiency of the pesticide application to *Cydia pommonella*.

TABLE 6

agent	pesticide action on <i>Cydia pommonella</i> (%)
10% pesticide	81.4
10% pesticide + 0.3% of Mitac-20	86.2
0.3% Mitac-20	82.5

*Example 11*

**Application against *Lobesia botrana*, *Eupoecillia ambiguella***

There were used a 15% aqueous pesticide solution prepared from the pesticide formulation according to Example 1 and a 0.3% solution of the commercial chemical pesticide Mitac-20 (active substance amitraz, CA 33089-61-1). The formulations were tested on adult vine plants (*Vitis vinifera*) of the sort "Kraljevina" infested with *Lobesia botrana*, *Eupoecillia ambiguella*.

The vine was grown in a commercial vineyard.

The efficiency of the application (calculation of efficiency) was measured according to Abbot's method.

The testing showed an efficiency of the pesticide application (insecticide action) in comparison with commercial pesticides.

Table 7 shows the efficiency of the pesticide application to *Lobesia botrana*, *Eupoecillia ambiguella*.

TABLE 7

agent	pesticide action on <i>Lobesia botrana</i> , <i>Eupoecillia ambiguella</i> (%)
15% pesticide	80.3
0.3% Mitac-20	89.5

### Example 12

#### Application against *Botrytis cinerea*

A 20% aqueous pesticide solution prepared from the pesticide formulation according to Example 1 was applied to adult vine plants (*Vitis vinifera*) of the sort "Kraljevina" infested with *Botrytis cinerea*.

The vine was grown in a commercial vineyard.

The efficiency of the pesticide application (calculation of efficiency) was measured according to Abbot's method.

The testing showed an efficiency of the pesticide application (fungicide action).

Table 8 shows the efficiency of the pesticide application to *Botrytis cinerea*.

TABLE 8

agent	pesticide action on <i>Botrytis cinerea</i> (%)
20% pesticide	54.4

*Example 13***Application against *Plasmopara viticora* without chemical pesticides and in combination therewith**

There were used pesticide formulations disclosed in Example 5, a 0.25% solution of the commercial chemical pesticide Dithane M45 (active substance mancozeb, CA 8018-01-7) as well as a combination of a 10% solution of the pesticide according to the invention to which 0.25% of Dithane M45 were added. The formulations were tested on vine (*Vitis vinifera*) infested with *Plasmopara viticora*.

The vine was grown in a commercial vine nursery.

The efficiency of the application (pesticide efficiency calculation) was measured according to Abbot's method.

The pesticide showed a very good fungicide action. In the combination with Dithane M45 a definite synergistic action of both agents occurred.

Table 9 shows the efficiency of the pesticide application to *Plasmopara viticora*.

**TABLE 9**

agent	pesticide action on <i>Plasmopara viticora</i> (%)
20% pesticide	51.3
10% pesticide	25.7
0.25% Dithane M45	62.0
10% pesticide + 0.25% of Dithane M45	85.6

*Example 14***Application against *Uncinula necator* without chemical pesticides and in combination therewith**

There were used pesticide formulations disclosed in Example 5, a 0.038% solution of the commercial chemical pesticide Topas 100 EC (active substance penconazole, CA 66246-88-6), a combination of a 10% solution of the pesticide according to the invention to which 0.038% of Topas 100 EC were added, a 0.5% solution of the commercial chemical pesticide Pepelin (active substance sulphur) as well as a combination of 10% solution of the pesticide according to the invention to which 0.5% of Pepelin were added. The formulations were tested on adult vine plants (*Vitis vinifera*) of the sort "Chardonnay" infested with *Uncinula necator*.

The vine was grown in a commercial vineyard.

The efficiency of pesticide application (efficiency calculation) was measured according to Abbot's method.

The pesticide showed a very good fungicide action. In the combination with Topas 100 EC or with Pepelin a definite synergistic action of both agents occurred.

Table 10 shows the efficiency of pesticide application to *Uncinula necator*.

**TABLE 10**

agent	pesticide action on <i>Uncinula necator</i> (%)
20% pesticide	58.3
10% pesticide	41.1
10% pesticide + 0.038% of Topas 100 EC	82.1
0.038% Topas 100 EC	76.1
10% pesticide + 0.5% of Pepelin	77.4
0.5% Pepelin	63.9



## CLAIMS

1. A non-toxic biodegradable pesticide composition *comprising*
  - as an active substance a modified starch having the reduction number between 2 and 10, preferably between 4 and 7, which is the product of an acid/thermic hydrolysis of natural starches, especially potato starch, under interrupting the hydrolysis by rapid cooling;
  - a surfactant for regulating adhesion and
  - a preservative.
2. The use of a pesticide composition according to claim 1 as a physico-mechanical pesticide having an insecticide, acaricide and fungicide action for controlling different kinds of plant pests.
3. A pesticide composition *comprising* a pesticide composition according to claim 1 in combination with chemical insecticides, acaricides and fungicides, which composition provides for a synergistic and prolonged action.

A. CLASSIFICATION OF SUBJECT MATTER  
 IPC 6 A01N25/14 A01N43/16 A01M1/14

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 A01N A01M

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US,A,5 110 804 (MERLIN LEE) 5 May 1992 see the whole document ---	1-3
X	WO,A,90 00351 (AQUASPERSIONS LIMITED) 25 January 1990 see page 4, line 21-27; claims ---	1-3
A	US,A,5 089 266 (MERLIN LEE) 18 February 1992 -----	

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☒ Patent family members are listed in annex.

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Patent document cited in search report	Publication date	Patent family member(s)		Publication date
US-A-5110804	05-05-92	AU-A-	5002890	18-04-91
		WO-A-	9312653	08-07-93
		GR-A-	90100735	20-03-92
-----				
WO-A-9000351	25-01-90	AU-B-	633504	04-02-93
		AU-A-	3983589	05-02-90
		DE-D-	68910212	02-12-93
		DE-T-	68910212	03-03-94
		EP-A-	0352010	24-01-90
		EP-A-	0424454	02-05-91
		GB-A, B	2239602	10-07-91
		JP-T-	3505876	19-12-91
US-A-	5140017	18-08-92		
-----				
US-A-5089266	18-02-92	AU-A-	5002790	18-04-91
		GR-A-	90100734	20-03-92
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